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<p>(21) Serial number of international application : PCT/FR97/00055</p> <p>(22) Date of international registration : January 14, 1997 (14.01.97)</p> <p>(30) Priority data : 96/00380 January 15, 1996 (15.01.96) FR</p> <p>(71) Applicant (for all countries mentioned except the U.S.) : ARJO WIGGINS S.A. [FR/FR] ; 117, quai du Président-Roosevelt, F-92130 Issy-les-Moulineaux (FR).</p> <p>(72) Inventors ; and</p> <p>(75) Inventors / Applicants (US only) : MAGNIN, Henri [FR/FR] ; Le Guillermet, F-38850 Charavines (FR). PERRIN, Claude [FR/FR] ; 375, rue du Bois, F-38140 Apprieu (FR), CAULET, Pierre [FR/FR] ; Le Bas Guillermet, F-38850 Charavines (FR).</p> <p>(74) Agent : DOMANGE, Maxime : Arjo Wiggins S.A., 177, quai du Président-Roosevelt, F-92442 Issy-les- Moulineaux Cédex (FR).</p>		<p>(81) Designated states / countries : BR, CA, CN, JP, PL, US, European Patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>With report on international search.</i></p>

A paper-based sheet comprising abrasive particles which, in use, impart high abrasion resistance thereto is disclosed. The sheet comprises abrasive particles coated with a non-abrasive material, particularly a polymer. The particles are selected from alumina, silica, boron nitride, silicon carbide, titanium carbide, tungsten carbide, zirconium oxide, cerium oxide, glass and ceramic particles or mixtures thereof. Laminates comprising said sheet and methods for making such sheets and laminates are also disclosed.

ABRASION-RESISTANT PAPER-BASED SHEET AND LAMINATES

The invention relates to paper-based sheet comprising abrasive particles which, in use, impart a high abrasion resistance to it. Such sheet is employed especially in manufacture of laminates, imparting to them an increased surface abrasion resistance. The invention also relates to laminates comprising it and to the processes of manufacturing the sheets and laminates.

For many years, laminates have been in use as materials for living and working spaces. Typical applications of such laminates are floor coverings, in particular those imitating parquet, linings and coatings of furniture, table tops, chairs and others. As a consequence they are subjected to much rubbing and chafing which abrades their surface; a desirable property of these laminates is therefore a high abrasion resistance, especially as regards floor coverings.

Abrasion resistance can be characterized by the so-called TABER resistance, measured according to the NF-EN 483-2 (1991) standard and expressed in number of turns.

For intensive household use of a laminate its abrasion resistance should correspond to a TABER resistance of at least 4000 turns, and must attain 10,000-12,000 turns for use in public places.

Of decorative panels there exist several types: the so-called high-pressure panels, the so-called low-pressure panels, and the sheet-covered panels which have a finish sheet stuck onto them.

The so-called high-pressure laminates are made from a base constituted of resin-impregnated sheets. These sheets are generally Kraft paper impregnated with a thermosetting resin, usually a phenolic resin. After being impregnated with resin, the sheets are dried, cut to size, and stacked. The number of sheets in the stack depends on the intended use and varies between 3 and 9, although it may be higher than that.

Then, on the stack of sheets that constitutes the base, a decorative sheet is placed. Such a sheet is generally a paper sheet carrying a pattern, imprinted or colored, or comprising decorative particles, impregnated with a thermosetting resin that does not darken during exposure to heat, e.g. melamine-formaldehyde resin, benzoguanamine-formaldehyde resin, unsaturated polyester resin; sometimes this sheet is not impregnated, the resin being provided by creep flow of resin from adjoining sheets. Generally, on top of the decorative sheet

a protective cover sheet is placed, without a pattern and transparent in the final laminate; in professional parlance this protective sheet is called "over-lay" or "overlay". Next the stack of impregnated sheets is placed in a laminating press whose plates are fitted with sheetings that are to impart the desired surface condition to the laminate. The stack is now densified by being compressed at a temperature in the 110°C to 170°C temperature range under a pressure in the 5.5 MPa to 11 MPa range, for around 25 to 35 minutes, so as to obtain a unified structure.

This structure is then fixed on a support; e.g., it is stuck onto a particle-board panel.

The so-called low-pressure laminates are produced by using only a decorative sheet, impregnated with thermosetting resin, and, where appropriate, an overlay, and laminating directly on the support in a short cycle, during which the temperature is of the order of 160 to 175°C and the pressure is 1.25 MPa to 1.6 MPa.

The third type of decorative panel comprises panels composed of a support - generally a particle-board or fiberboard panel - and a decorative paper sheet impregnated with a formula containing a binder or a melamine-formaldehyde resin and a polymer, fixed onto the support by means of an adhesive.

In this case the paper sheet is a decorative sheet of uniform color or patterned. The color or the pattern is usually applied by imprinting on the sheet, before or after impregnation. Additionally a varnish or lacquer is applied to protect the surface of the sheet. An example of such a sheet, called a finishing sheet or impregnated sheet, and the decorative panel comprising it, are described in patent application WO-A-9517551.

The protective sheet known as "overlay" is traditionally produced by draining an aqueous suspension of only slightly refined cellulose fiber. Such a sheet has a low per-area weight which is comprised between 10 and 50 g/m², and is not frosted. It is impregnated with a thermosetting resin, which ensures its clarification in the final laminate and allows the pattern of the laminate to shine through. The resin is mostly selected from among melamine, urea or unsaturated polyester resins.

This overlay sheet protects the surface of the laminate, increasing in particular its abrasion resistance by the additional contribution of thermosetting resin.

In order to have a very high abrasion resistance, an overlay of large per-area weight must be employed which, however, impairs the visibility of features through the overlay.

This is the most current method for enhancing the abrasion resistance of laminates.

This resistance may, however, be even further increased by employing particles of high abrasivity and thus high abrasion resistance, known in professional parlance as abrasive particles. Their abrasive nature is due to their hardness and their shape which presents many ridges. These particles are present in or on the "overlay" or on the patterned sheet itself.

In order not to affect the transparency of the overlay after impregnation, they must on the one hand be transparent or translucent, or white or grayish white, and must on the other hand not have a too large average size, preferably not exceeding 200 μm , and should not occur in too great amount.

Yet in order to achieve a high abrasion resistance it is desirable to have the particles as large as possible and / or add them in large numbers.

In the above sense the utilization has been described of very hard inorganic particles e.g. alumina or corundum, silica including quartz, boron nitride, silicon carbide, titanium carbide, tungsten carbide; their Mohs hardnesses are comprised between 3 and 10, but may be higher [sic]. These particles have been cited in many patents, particularly in GB-A-1139183, GB-A-1378879, DE-A-2107091, FR-A-2104707, FR-A-2139990, US-A-3661673, US-A-5141799 and CA 836522.

These particles can be introduced into or onto the paper sheet:

- either by blending into the pulp during production of the sheet; however, owing to their abrasive character the paper machine wears fast; another inconvenience is that the particles are not well retained in the paper,
- or by depositing from a second feed box on the paper machine, but the machine still undergoes wear;
- or by impregnation or coating simultaneously with the impregnating resin, after having been mixed with the latter and, as the case may be, after imprinting of the sheet if it is a decorative sheet, but an inconvenience is that the mixture does not readily lend itself to good homogenization, thus segregation of particles can occur which causes them to hold insufficiently on the sheet,
- or by deposition, in particular by electrostatic spraying, on the sheet, pre-impregnated with resin; this process, described in Patent FR-B-2104707, registered in 1970, to remedy the inconveniences of the prior art, reduces the number of production machines suffering from wear; however, the spraying is not easily kept uniform and creates a dusty atmosphere.

And in any event, whatever the process of incorporation of abrasive particles, there is always the rapid wear of the laminating machines, in particular the sheetings on the plates of the laminating press.

An inconvenience of this wear of the press sheetings is that the surface condition which they impart to the laminate is altered too. This thwarts especially the obtaining of high-gloss laminates because the gloss is principally conditioned by the surface; in this way it is therefore not possible to produce high-gloss laminates that are very abrasion-resistant.

For more than twenty-five years attempts have thus been made at introducing so-called abrasive particles into or onto cellulosic sheet, without, however, succeeding in preventing wear of machinery for producing sheets and / or laminates.

On the other hand, particles are known, particularly through patent applications as specified further below, which present a certain abrasivity and which have been coated more or less completely with another material. Thus in French patent application FR-A-1543107, registered in 1967, coatings are described which comprise waxes, paraffins or fatty alcohols, to coat solid products employed as additives to plastics or resins. Such coating diminishes the abrasive effect of the solid products, in particular titanium oxide, on the plastic or resin processing equipment. This patent application therefore does not pertain to paper-based sheet nor to the obtaining of abrasion-resistant products.

In British patent application GB-A-1574068, registered in 1976, the coating has been described of products such as fibers, pigments or micro-capsules by a discrete layer of regenerated cellulose. This treatment diminishes the wear of the web of the paper machine from these products, through improved retention of the products. The principle here is that of maintaining as much as possible of the material within the sheet as it is being created, thus reducing the extent of deposition of products on the paper machine web which then wears less. Thus the aim is not that the coating material actually reduce the abrasivity of the particles, and even less that it be restored later on.

In Japanese patent JP-B-93007063 by MITSUBISHI, mineral particles are described, among them alumina or silica particles, which are encapsulated in a polymer selected from among, in particular, polystyrene and derivatives, polymers of (meth)acrylic acid or its alkyl esters, polyacrylamides, polyacrylonitriles, poly(vinyl acetate).

In Japanese patent application JP-A-05015772 by NIPPON JUNYAKU, mineral particles are described, among them alumina or silica particles, which are encapsulated in a copolymer of (meth)acrylic acid and vinylic monomer.

In patent applications EP-A-380428 or EP-A-505230 by RHONE POULENC, the coating of mineral particles with organopolysiloxanes has been described. The purpose here is to load the latex with organopolysiloxanes to improve the mechanical characteristics of the latex, it having been found that charging in the form of encapsulated entities makes for synergism and compatibility between the load and the latex. Thus one is not dealing with an attempt to counter the abrasivity of mineral fillers.

In the prior art expounded above, the coating treatment of the particles was executed by the professional with the purpose of their permanent encapsulation, and was not aimed at obtaining a sheet containing these particles and having heightened abrasion resistance and / or imparting such resistance to the surface of a product comprising it, during its use.

The invention sets out to resolve the problems of the prior art for producing abrasion-resistant sheets through incorporation of very abrasive charges, and laminates that comprise them.

The main objective of the invention is to furnish a paper-based sheet, in particular for the manufacture of decorative laminates, such sheet carrying abrasive particles and having very high abrasion resistance and / or imparting such resistance to the product that comprises it, and wherein the production of the sheet and / or of the product comprising it does not cause rapid wear of the paper machines and / or the machine(s) for manufacturing the product; this latter item referring in particular to the sheetings on the laminating presses.

Another objective is that the distribution of the particles be uniform.

Another objective is that the abrasive particles not impair the transparency or the decorative effect of the sheets containing them.

A secondary objective is that the abrasive particles be well retained in, or bound to, the paper.

The Body of Applicants have found that the principal aim of the invention is achieved when use is made of abrasive particles coated in a layer of non-abrasive material.

By "non-abrasive material" is understood a material less hard than the particles to be coated, and which, applied as a surrounding layer, reduces the number and the extent of protrusion of the ridges forming part of the morphology of the particles.

The coated abrasive particles have characteristically an EINLEHNER abrasivity, determined by the test described in example 1 below, that is smaller than that of the non-coated particles.

This coating material functions by sufficiently diminishing the abrasive character of the non-coated particles so as to reduce, through this fact of being coated, the wear of the machines during the production of the paper-based sheet, as also the wear of the machines that assemble the products which comprise the sheet. Moreover this coating does not impair the abrasion resistance of the paper-based sheet, for when this is subsequently subjected to wear, the coating does not resist the abrasion and wears off on the abrasion-exposed parts of the particles, such that the abrasion resistance of the sheet based on the presence of the abrasive particles can come out.

Thus the coating is, at least in part, temporary and serves to delay the abrasive effect of the particles.

Indeed within the scope of the present invention, on the one hand the coating prevents wear of the machines in producing the sheet or the laminate, and on the other hand when the resulting laminate is exposed to wear [this too is curbed].

Although coated fillers are known in prior art as described above, and although attempts have been made during more than twenty-five years at reducing the wear of the machines that produce these charged sheets and laminates, especially in the field of decorative laminates, those versed in the art have never as yet considered the solution proposed by the present invention.

The professional who has as his aim to develop an end product resisting to abrasion thanks to the abrasive nature of the particles, has not given thought to initially suppressing or at least diminishing this abrasive effect of the particles.

In particular the non-abrasive coating material is a polymer. This polymer may be a natural or a synthetic one.

Also the coating material, according to its ionicity, can contribute to better retention of the particles; this ionicity may be regulated during the production of synthetic polymers.

The invention furnishes a paper-based sheet carrying abrasive particles which, in use, impart to it an enhanced abrasion resistance, carrying them encapsulated in a non-abrasive material.

More specifically the sheet of the invention is characterized in that the coated abrasive particles have an EINLEHNER abrasivity, determined according to the test described in example 1 below,

that is smaller than, or equal to, 55 g/m^2 . Preferably this EINLEHNER abrasivity is smaller than or equal to 20 g/m^2 .

In particular the sheet of the invention is characterized in that the so-called abrasive particles are chosen from among particles of alumina, silica, boron nitride, silicon carbide, titanium carbide, tungsten carbide, zirconium oxide, cerium oxide, glass, ceramics, or their mixtures. Preferably the particles are alumina.

The particles may have different shapes; they may e.g. be spherical, or essentially spherical, polyhedral, or even fiber-shaped; preferably these particles, prior to being coated, carry numerous ridges.

In an embodiment, the size of the coated abrasive particles is comprised between 10 and 200 μm , preferably between 20 and 150 μm .

Preferably the so-called abrasive particles, prior to coating, have a Mohs hardness of at least 6.

More in particular the coating material must be optically compatible with the intended use of the sheet comprising it, i.e. it must not interfere with the transparency of the sheet when the latter is an overlay or, when the sheet is a decorative one, it must be compatible with that purpose. Moreover it must not turn yellow when subjected to the temperature for joining together the sheets into a laminate; nor must it yellow over time.

The coating material must be transparent to translucent, or white to grayish white, so as not to alter the visual aspect of the sheet that comprises it, especially when this sheet serves as an overlay and is thus supposed to be transparent.

In an embodiment of the invention, the non-abrasive material is a polymer.

In an embodiment of the invention the coating polymer is chosen among organopolysiloxanes, homo- or copolymers of styrene and its derivatives, homo- or copolymers of acrylic acid or esters, homo- or copolymers of methacrylic acid or esters including poly(methyl methacrylate), vinylic homo- or copolymers, polyolefins, polysaccharides including ethylcellulose.

Among polysaccharides, applicable ones are cellulose derivatives such as ethylcellulose or a product like chitin, in particular obtained from crustaceans' carapaces.

The polymer is preferably chosen from polystyrene, poly(methyl methacrylate) and ethylcellulose.

Preferably the coating material represents 1 to 10 % by dry weight, referred to the dry weight of the coated particles.

The sheets can be impregnated or covered by means of a composition, in particular by means of a thermosetting resin.

In an embodiment of the invention, the sheet is characterized in that it comprises a thermosetting resin, and more specifically in that the thermosetting resin is chosen among melamine, benzoguanine, unsaturated polyester and urea resins.

More specifically the sheet according to the invention is characterized in that it comprises, on a dry weight basis, between 1 and 70 %, preferably between 20 and 40 %, of coated abrasive particles, referred to total weight, excluding the weight of the thermosetting resin if present.

The sheet according to the invention can be used as a protective sheet, a so-called "overlay". The sheet is placed on the decorative sheet of the laminate.

An advantage is found in the fact that this sheet may constitute an overlay of low per-area weight, yet contributing a large abrasion resistance, without impairing the visibility of the patterned laminate under it.

The invention also pertains to an overlay for abrasion-resistant laminates characterized in that they carry it with the coated abrasive particles included.

In another embodiment the sheet of the invention can itself be used as a decorative sheet on the laminate. The invention also relates to a decorative sheet for abrasion-resistant laminates characterized in that they carry it with the coated abrasive particles included.

The sheet according to the invention is obtained in the papermaking mode, from a dispersion on the basis of cellulose fibers in aqueous medium, the coated abrasive particles being blended into the cellulose fibers. The dispersion preferably comprises a wet strength agent.

In the case of a sheet for decorative purposes the dispersion may additionally carry frosting or coloring pigments.

The sheet can, if required, be built up in consecutive squirts, the top one containing the coated abrasive particles.

The invention also pertains to a process for production of a paper-based sheet according to the invention, wherein the abrasive particles, coated in the said non-abrasive substance, are introduced into or onto the sheet.

And in particular the invention pertains to the process for production, in the papermaking mode, of the sheet based on cellulose fiber, characterized in that, in the paper machine's feed box containing the cellulose fibers, the abrasive particles, covered by the non-abrasive material, are incorporated by blending.

The invention also pertains to another embodiment of the process of production of the cellulose-fiber-based sheets in the papermaking mode, characterized in that the abrasive particles, coated by the non-abrasive substance, are added onto the surface of the sheet being wet-formed, from another feed box on the paper machine.

The coated abrasive particles may also be introduced using other techniques, as previously mentioned, in particular by methods of impregnation, especially in a mixture with a so-called impregnating resin, or by methods of surface deposition. In particular the procedures of surface deposition, especially by topping or spraying, can be utilized on a sheet pre-impregnated with a thermosetting resin, and pre-imprinted in the case of a decorative sheet. In all of these instances the coated condition of the particles prevents wear of the machinery employed.

The sheet according to the invention can also be a decorative sheet called a finishing sheet, serving as the concluding element in the third type of decorative panels defined in the introductory part of this document. This sheet can advantageously be imprinted without wear to the printing machines.

The invention pertains also to an abrasion-resistant laminate characterized in that it carries as the "overlay" a sheet according to the invention.

The invention pertains moreover to an abrasion-resistant laminate characterized in that it carries as the decorative sheet a sheet according to the invention.

In an embodiment of the invention the laminate carrying the sheet comprising the coated particles is characterized in that its TABER abrasion resistance, measured according to the NF-EN-483-2 (1991) standard, is greater than, or equal to, 3000 turns.

If desired, the laminate may carry as a decorative sheet the sheet according to the invention, plus a classical "overlay" (not containing abrasive particles) for even greater resistance to abrasion.

In yet another option the laminate may carry a decorative sheet and an "overlay" both according to the invention, for still greater resistance to abrasion.

In an embodiment of the invention the laminate is characterized in that it has a high gloss. The high gloss is obtained thanks to the surface condition of the sheetings on the laminating press not being affected by the action of the abrasive particles as they are covered under the non-abrasive substance.

The invention relates also to the manufacturing of a laminate characterized in that on the stack of various components of the laminate at least one sheet is placed that comprises the coated abrasive particles and all these elements are then pressed together.

In the case of a so-called high-pressure laminate the laminate components other than the sheet with the coated abrasive particles are the thermoset-impregnated Kraft sheets and the decorative sheet, which may be thermoset-impregnated in the event that this decorative sheet does not contain the coated abrasive filler particles.

In the case of a low-pressure laminate the laminate components other than the sheet with the coated abrasive particles are the support panel being represented by a particle-board panel and a decorative sheet impregnated with a thermosetting resin, in the event that this decorative sheet does not contain the coated abrasive filler.

The non-restrictive examples that follow, will enable to better understand the invention:

EXAMPLE 1. COMPARATIVE :

A reference sheet is made with uncoated abrasive alumina particles. These alumina particles are of KNOOP hardness 2100 i.e. MOHS hardness 9; their average size is 100 μm .

The employed alumina particles are characterized by an EINLEHNER abrasivity of 86 g/m^2 .

By way of comparison: the EINLEHNER abrasivity of titanium oxide particles, which are among the most abrasive paper fillers in current use, is 14 g/m^2 .

The EINLEHNER abrasivity of the particles is determined under the following test specifications:

The pigment is oven-dried at 105°C for 24 hours, then 10 g of it is suspended in 1000 g of distilled water. Its pH is adjusted to 6 with aluminium sulfate.

The principle of the measurement consists in circulating the test sample particles between a moving part and a metallic grid, under vigorous agitation. The standard duration of the test is 120 minutes, but with very abrasive products it may have to be shortened, since the weight loss of the gauze must not exceed 40 mg i.e. 130 g/m².

In the present case, the samples to be tested being very abrasive, the duration of test is fixed at 30 minutes.

The abrasivity of the test product is given by the weight loss of the metal gauze per m², and is found in g/m² by the following formula:

$$\text{Einlehner abrasivity} = X \cdot 10^{-3} / 305 \cdot 10^{-6}$$

where X is the weight difference, in milligrams, of the gauze before and after abrasion, and $305 \cdot 10^{-6}$ is the surface of the abrasion-exposed gauze in m².

A reference overlay is made using a Fourdrinier-type paper machine, from an aqueous composition of cellulose fiber refined to 20°SR (degrees SCHOEPPER-RIEGLER). The alumina particles are blended into the fiber. The sheet contains furthermore 2 weight % of a wet-strength agent on the basis of melamine-formaldehyde resin.

The dried sheet has a per-area weight of 43 g/m².

The ash content is determined according to ISO standard 2144 (1987) at 420°C; the sheet is found to contain approx. 8.6 % of mineral constituents, chiefly representing the alumina, the remainder being mineral residues contained in the pulp and brought in with the additives.

The sheet is impregnated with melamine-formaldehyde resin in aqueous medium, the extent of impregnation being 72 % i.e. 72 dry-weight grams of resin per 100 grams of impregnated paper.

This sheet is laminated so as to manufacture a high-pressure laminate, by the following method and under the following operating conditions: 5 sheets of Kraft paper, impregnated with phenol resin, are stacked, and are then topped with an imprinted decorative sheet impregnated with melamine-formaldehyde resin, and finally the impregnated overlay sheet is placed.

The plates of the laminating press are heated to 160°C and a pressure of 6.9 MPa (70 kg/cm²) is applied, during 30 minutes.

The abrasion resistance of the obtained laminate is measured according to section 6 of the NF-EN 438-2 (1991) standard. This resistance is expressed in the average wear R which is of the order of 4300 turns.

EXAMPLE 2 :

The reference alumina particles are coated by placing them in suspension in a fluidized bed and vaporizing [sic] into it a dichloromethane solution of the polymer, poly(methyl methacrylate). The result is approx. 1.5 weight % of polymer on the coated particles.

The size of the coated particles is essentially the same as that of the bare ones; they have been covered with a thin film of polymer. Under a scanning electron microscope a check is made that the alumina particles are entirely surrounded by film.

The EINLEHNER abrasivity of the coated particles is measured under the identical conditions as in the comparative example. It is found at 45 g/m^2 , and is thus substantially lower than in the reference.

As with the reference, an overlay is made, on a Fourdrinier paper machine, from an aqueous-medium composition of cellulose fiber refined to 20°SR (degrees SCHOEFFER-RIEGLER). Into the fiber there is blended an alumina particulate as in the [previous] example but this time coated with the poly(methyl methacrylate). The sheet also contains 2 %, on a dry-weight basis, of a wet-strength agent based on melamine-formaldehyde resin.

The dried sheet has a per-area weight of 38 g/m^2 .

The ash content is determined according to ISO standard 2144 (1987) at 420°C ; the sheet is found to contain approx. 10 % of mineral constituents, chiefly representing the alumina, the remainder being mineral residues contained in the pulp and brought in with the additives.

The sheet is impregnated with melamine-formaldehyde resin in aqueous medium, the extent of impregnation being 70 % i.e. 70 dry-weight grams of resin per 100 grams of impregnated paper.

This sheet is laminated into a high-pressure laminate, by the method and under the operating conditions of comparative example 1.

The abrasion resistance of the resulting laminate is measured according to section 6 of the NF-EN 438-2(1991) standard. This resistance, given by the average wear R, is of the order of 4500 turns. Thus the resistance has been preserved, compared to the reference of comparative example I.

It is visually checked that the coating polymer has not yellowed during the laminating.

It is also checked that the presence of the coated filler particles has not reduced the transparency of the sheet containing them, as compared to the reference, and that the decorative effect of the laminate has not been affected.

It is also checked that the mechanical characteristics (tensile strength, wet strength) and the porosity of the paper sheet have been preserved, compared to the reference.

EXAMPLE 3:

The reference alumina particles are coated by being placed in suspension in a fluidized bed and vaporizing into this a toluene solution of the polymer, polystyrene. This results in an approx. 2.5 weight % deposit of polymer film on the particles.

The size of the coated particles is essentially equal to that of the bare particles; they have been covered with a thin film of polymer. Under a scanning electron microscope it is checked that the alumina particles are completely surrounded by film.

The EINLEHNER abrasivity of the coated particles is determined by measuring under the same conditions as for the reference. It is found at 15 g/m^2 , thus at the same level as that of titanium oxide particles, and hardly more than a sixth of that of the reference.

Like in the cases of the reference and example 2, an overlay sheet is produced with a Fourdrinier-type paper machine, from an aqueous-medium composition of cellulose fiber refined to 20°SR (degrees SCHOEPPER-RIEGLER). Into the fiber are blended polystyrene-coated alumina particles. The sheet contains additionally 2 %, by dry weight, of a wet-strength agent based on melamine-formaldehyde resin.

The dried sheet has a per-area weight of 38 g/m^2 .

The ash content is determined according to ISO standard 2144 (1987) at 420°C; the sheet is found to contain approx. 9 % of mineral constituents, chiefly representing the alumina, the remainder being mineral residues contained in the pulp and brought in with the additives.

The sheet is impregnated with melamine-formaldehyde resin in aqueous medium, the extent of impregnation being 73 % i.e. 73 dry-weight grams of resin per 100 grams of impregnated paper.

This sheet is laminated into a high-pressure laminate, by the method and under the operating conditions of comparative example 1.

The abrasion resistance of the resulting laminate is measured according to section 6 of the NF-EN 438-2(1991) standard. This resistance, given by the average wear R, is of the order of 4000 turns. Thus the resistance has been preserved, compared to the reference of comparative example 1.

It is visually checked that the coating polymer has not yellowed during the laminating.

It is also checked that the presence of the coated filler particles has not reduced the transparency of the sheet containing them, as compared to the reference, and that the decorative effect of the laminate has not been affected.

It is also checked that the mechanical characteristics (tensile strength, wet strength) and the porosity of the paper sheet have been preserved, compared to the reference.

EXAMPLE 4 :

The reference alumina particles are coated by being placed in suspension in a fluidized bed and vaporizing into this a toluene solution of the polymer, ethylcellulose. This results in an approx. 1.5 weight % deposit of polymer film on the particles.

The size of the coated particles is essentially equal to that of the bare particles; they have been covered with a thin film of polymer. Under a scanning electron microscope it is checked that the alumina particles are completely surrounded by film.

The EINLEHNER abrasivity of the coated particles is determined by measuring under the same conditions as for the reference. It is found at 55 g/m^2 , thus substantially lower than that of the reference.

Like in the case of the reference, an overlay sheet is produced with a Fourdrinier-type paper machine, from an aqueous-medium composition of cellulose fiber refined to 20°SR (degrees SCHOEPPER-RIEGLER). Into the fiber are blended alumina particles of the previous example, this time coated in ethylcellulose. The sheet contains additionally 2 %, by dry weight, of a wet-strength agent based on melamine-formaldehyde resin.

The dried sheet has a per-area weight of 38 g/m^2 .

The ash content is determined according to ISO standard 2144 (1987) at 420°C ; the sheet is found to contain approx. 10 % of mineral constituents, chiefly representing the alumina, the remainder being mineral residues contained in the pulp and brought in with the additives.

The sheet is impregnated with melamine-formaldehyde resin in aqueous medium, the extent of impregnation being 70 % i.e. 70 dry-weight grams of resin per 100 grams of impregnated paper.

This sheet is laminated into a high-pressure laminate, by the method and under the operating conditions of comparative example 1.

The abrasion resistance of the resulting laminate is measured according to section 6 of the NF-EN 438-2(1991) standard. This resistance, given by the average wear R, is of the order of 4500 turns. Thus the resistance has been preserved, compared to the reference of comparative example 1.

It is visually checked that the coating polymer has not yellowed during the laminating.

It is also checked that the presence of the coated filler particles has not reduced the transparence of the sheet containing them, as compared to the reference, and that the decorative effect of the laminate has not been affected.

It is also checked that the mechanical characteristics (tensile strength, wet strength) and the porosity of the paper sheet have been preserved, compared to the reference.

SCOPE OF PATENT CLAIMS

1. A paper-based sheet comprising abrasive particles which impart to it, in use, a high abrasion resistance, characterized in that the sheet carries the said abrasive particles coated in a non-abrasive coating material.

2. The sheet of claim 1, characterized in that the non-abrasive coating material is a polymer.

3. The sheet of claim 1 or 2, characterized in that the EINLEHNER abrasivity of the coated abrasive particles, according to the test described in example 1 of the descriptive part, is lower than or equal to 55 g/m².

4. The sheet of any of claims 1 through 3, characterized in that the particles are chosen among particles of alumina, silica, boron nitride, silicon carbide, titanium carbide, tungsten carbide, zirconium oxide, cerium oxide, glass, ceramic material, or their mixtures.

5. The sheet of any of claims 1 through 4, characterized in that the size of the coated abrasive particles is comprised between 10 and 200 µm, preferably between 20 and 150 µm.

6. The sheet of any of claims 1 through 5, characterized in that the abrasive particles, before being coated, have a Mohs hardness of at least 6.

7. The sheet of any of claims 2 through 6, characterized in that the coating polymer is chosen from among organopolysiloxanes, homo- or copolymers of styrene and its derivatives, homo- or copolymers of acrylic acid or esters, homo- or copolymers of methacrylic acid or esters including poly(methyl methacrylate), vinylic homo- or copolymers, polyolefins, polysaccharides including ethylcellulose.

8. The sheet of claim [2 through] 7, characterized in that the coating polymer represents, on a dry weight basis, 1 to 10 % referred to the coated particles.

9. The sheet of any of claims 1 through 8, characterized in that it comprises a thermosetting resin.

10. The sheet of claim 9, characterized in that the resin is selected among melamine, benzoguanamine, unsaturated polyester and urea resins.

11. The sheet of any of claims 1 through 10, characterized in that it comprises between 1 and 70 %, preferably between 1 and 40 %, of the said coated particles, expressed as dry weight per total dry weight excluding the thermosetting resin when applicable.

12. An overlay sheet for abrasion-resistant laminates, characterized in that it embodies a sheet according to any of claims 1 through 11.

13. A decorative sheet for abrasion-resistant laminates, characterized in that it embodies a sheet according to any of claims 1 through 11.

14. An abrasion-resistant laminate, characterized in that it carries as the overlay a sheet according to claim 12.

15. An abrasion-resistant laminate, characterized in that it carries as the decorative sheet a sheet according to claim 13.

16. The laminate of claim 14 or 15, characterized in that its TABER abrasion resistance, measured according to the NF-EN-483-2 (1991) standard, equals at least 3000 turns.

17. The laminate of any of claims 14 through 16, characterized in that it has a high gloss.

18. A process for manufacture of the paper-based sheet of any of claims 1 through 13, characterized in that the said abrasive particles are incorporated into the sheet, having been coated with the said non-abrasive material.

19. A process for manufacturing from cellulose fiber, in the papermaking fashion, a sheet corresponding to any of claims 1 through 13, characterized in that, in the feed box on the paper machine which contains the cellulose fibers, the said abrasive particles in the said coating are incorporated into the feed.

20. A process for manufacturing from cellulose fiber, in the papermaking fashion, a sheet corresponding to any of claims 1 through 13, characterized in that the said abrasive particles in the said coating are added from another feed box on the paper machine, onto the surface of the sheet as it is being wet-formed.

21. A process for manufacture of a laminate, characterized in that, onto the stack of laminate components, at least one sheet is placed that corresponds to any of claims 1 through 13 or has been obtained according to claim 18 or 19, and this (these) sheet(s), plus the other components of the laminate, are pressed together.